

January 14, 1869.

Lieut.-General SABINE, President, in the Chair.

The following communications were read :—

- I. "On the Relation of Hydrogen to Palladium." By THOMAS GRAHAM, F.R.S., Master of the Mint. Received November 23, 1868.

It has often been maintained on chemical grounds that hydrogen gas is the vapour of a highly volatile metal. The idea forces itself upon the mind that palladium with its occluded hydrogen is simply an alloy of this volatile metal, in which the volatility of the one element is restrained by its union with the other, and which owes its metallic aspect equally to both constituents. How far such a view is borne out by the properties of the compound substance in question will appear by the following examination of the properties of what, assuming its metallic character, would have to be named *Hydrogenium*.

1. *Density*.—The density of palladium when charged with eight or nine hundred times its volume of hydrogen gas is perceptibly lowered; but the change cannot be measured accurately by the ordinary method of immersion in water, owing to a continuous evolution of minute hydrogen bubbles which appears to be determined by contact with the liquid. However, the linear dimensions of the charged palladium are altered so considerably that the difference admits of easy measurement, and furnishes the required density by calculation. Palladium in the form of wire is readily charged with hydrogen by evolving that gas upon the surface of the metal in a galvanometer containing dilute sulphuric acid as usual*. The length of the wire before and after a charge is found by stretching it on both occasions by the same moderate weight, such as will not produce permanent distention, over the surface of a flat graduated measure. The measure was graduated to hundredths of an inch, and by means of a vernier, the divisions could be read to thousandths. The distance between two fine cross lines marked upon the surface of the wire near each of its extremities was observed.

Expt. 1.—The wire had been drawn from welded palladium, and was hard and elastic. The diameter of the wire was 0.462 millimetre; its specific gravity was 12.38, as determined with care. The wire was twisted into a loop at each end and the mark made near each loop. The loops were varnished so as to limit absorption of gas by the wire to the measured length between the two marks. To straighten the wire, one loop was fixed, and the other connected with a string passing over a pulley and loaded with 1.5 kilogramme, a weight sufficient to straighten the wire without occasioning any undue strain. The wire was charged with hydrogen by making it the negative electrode of a small Bunsen's battery consisting of two cells, each of half a litre in capacity. The positive electrode was a thick platinum wire placed side by side with the palladium wire, and

* Proceedings of the Royal Society, p. 422, 1868.

extending the whole length of the latter within a tall jar filled with dilute sulphuric acid. The palladium wire had, in consequence, hydrogen carried to its surface, for a period of $1\frac{1}{2}$ hour. A longer exposure was found not to add sensibly to the charge of hydrogen acquired by the wire. The wire was again measured and the increase in length noted. Finally the wire, being dried with a cloth, was divided at the marks, and the charged portion heated in a long narrow glass tube kept vacuous by a Sprengel aspirator. The whole occluded hydrogen was thus collected and measured; its volume is reduced by calculation to Bar. 760 millims., and Therm. 0° C.

The original length of the palladium wire exposed was 609·144 millims. (23·982 inches), and its weight 1·6832 grm. The wire received a charge of hydrogen amounting to 936 times its volume, measuring 128 cubic centims., and therefore weighing 0·01147 grm. When the gas was ultimately expelled, the loss as ascertained by direct weighing was 0·01164 grm. The charged wire measured 618·923 millims., showing an increase in length of 9·779 millims. (0·385 inch). The increase in linear dimensions is from 100 to 101·605, and in cubic capacity, assuming the expansion to be equal in all directions, from 100 to 104·908. Supposing the two metals united without any change of volume, the alloy may therefore be said to be composed of

	By volume.	
Palladium	100	or 95·32
Hydrogenium	4·908	or 4·68
	<hr/>	
	104·908	100

The expansion which the palladium undergoes appears enormous if viewed as a change of bulk in the metal only, due to any conceivable physical force, amounting as it does to sixteen times the dilatation of palladium when heated from 0° to 100° C. The density of the charged wire is reduced, by calculation, from 12·3 to 11·79. Again, as 100 is to 4·91, so the volume of the palladium, 0·1358 cubic centim., is to the volume of the hydrogenium, 0·006714 cubic centim. Finally, dividing the weight of the hydrogenium, 0·01147 grm., by its volume in the alloy, 0·006714 cubic centim., we find

Density of hydrogenium 1·708

The density of hydrogenium, then, appears to approach that of magnesium, 1·743, by this first experiment.

Further, the expulsion of hydrogen from the wire, however caused, is attended with an extraordinary contraction of the latter. On expelling the hydrogen by a moderate heat, the wire not only receded to its original length, but fell as much below that zero as it had previously risen above it. The palladium wire first measuring 609·144 millims., and which increased 9·77 millims., was ultimately reduced to 599·444 millims., and contracted 9·7 millims. The wire is permanently shortened. The density of the pal-

ladium did not increase, but fell slightly at the same time, namely from 12·38 to 12·12, proving that this contraction of the wire is in length only. The result is the converse of extension by wire-drawing. The retraction of the wire is possibly due to an effect of wire-drawing in leaving the particles of metal in a state of unequal tension, a tension which is excessive in the direction of the length of the wire. The metallic particles would seem to become mobile, and to right themselves in proportion as the hydrogen escapès; and the wire contracts in length, expanding, as appears by its final density, in other directions at the same time.

A wire so charged with hydrogen, if rubbed with the powder of magnesia (to make the flame luminous), burns like a waxed thread when ignited in the flame of a lamp.

Expt. 2.—Another portion of the same palladium wire was charged with hydrogen in a similar manner. The results observed were as follows:—

Length of palladium wire	488·976	millims.
Thesame with 867·15 volumes of occluded gas	495·656	„
Linear elongation	6·68	„
Linear elongation on 100	1·3663	„
Cubic expansion on 100	4·154	„
Weight of palladium wire	1·0667	gram.
Volume of palladium wire	0·08072	cub.centim.
Volume of occluded hydrogen gas	75·2	„
Weight of same	0·00684	gram.
Volume of hydrogenium	0·003601	cub.centim.
From these results is calculated .		
Density of hydrogenium	1·898.	

Expt. 3.—The palladium wire was new, and on this occasion was well annealed before being charged with hydrogen. The wire was exposed at the negative pole for two hours, when it had ceased to elongate.

Length of palladium wire	556·185	millims.
Same with 888·303 volumes hydrogen ..	563·652	„
Linear elongation	7·467	„
Linear elongation on 100	1·324	„
Cubic expansion on 100	4·025	„
Weight of palladium wire	1·1675	gram.
Volume of palladium wire	0·0949	cub. centim.
Volume of occluded hydrogen gas	84·3	cub. centims.
Weight of same	0·007553	gram.
Volume of hydrogenium	0·003820	cub. centim.
These results give by calculation		
Density of hydrogenium	1·977.	

It was necessary to assume in this discussion that the two metals do not

contract nor expand, but remain of their proper volume on uniting. Dr. Matthiessen has shown that in the formation of alloys generally the metals retain approximately their original densities*.

In the first experiment already described, probably the maximum absorption of gas by wire, amounting to 935·67 volumes, is attained. The palladium may be charged with any smaller proportion of hydrogen by shortening the time of exposure to the gas (329 volumes of hydrogen were taken up in twenty minutes), and an opportunity be gained of observing if the density of the hydrogenium remains constant, or if it varies with the proportion in which hydrogen enters the alloy. In the following statement, which includes the three experiments already reported, the essential points only are produced.

TABLE.

Volumes of hydrogen occluded.	Linear expansion in millimetres.		Density of Hydrogenium.
	From	To	
329	496·189	498·552	2·055
462	493·040	496·520	1·930
487	370·358	373·126	1·927
745	305·538	511·303	1·917
867	488·976	495·656	1·898
888	556·185	563·652	1·977
936	609·144	618·923	1·708

If the first and last experiments only are compared, it would appear that the hydrogenium becomes sensibly denser when the proportion of it is small, ranging from 1·708 to 2·055. But the last experiment of the Table it perhaps exceptional; and all the others indicate considerable uniformity of density. The mean density of hydrogenium, according to the whole experiments, excluding that last referred to, is 1·951, or nearly 2. This uniformity is in favour of the method followed for estimating the density of hydrogenium.

On charging and discharging portions of the same palladium wire repeatedly, the curious retraction was found to continue, and seemed to be interminable. The following expansions, caused by variable charges of hydrogen, were followed on expelling the hydrogen by the retractions mentioned.

	Elongation.		Retraction.	
1st Experiment	9·77	millims.	9·70	millims.
2nd „	5·765	„	6·20	„
3rd „	2·36	„	3·14	„
4th „	3·482	„	4·95	„
				23·99

The palladium wire, which originally measured 609·144 millims., has

* Philosophical Transactions, 1860, p. 177.

suffered, by four successive discharges of hydrogen from it, a permanent contraction of 23·99 millims. ; that is, a reduction of 3·9 per cent. on its original length. The contractions will be observed to exceed in amount the preceding elongations produced by the hydrogen, particularly when the charge of the latter is less considerable. With another portion of wire the contraction was carried to 15 per cent. of its length by the effect of repeated discharges. The specific gravity of the contracted wire was 12·12, no general condensation of the metal having taken place. The wire shrinks in length only.

In the preceding experiments the hydrogen was expelled by exposing the palladium placed within a glass tube to a moderate heat short of redness, and exhausting by means of a Sprengel tube ; but the gas was also withdrawn in another way, namely, by making the wire the positive electrode, and thereby evolving oxygen upon its surface. In such circumstances a slight film of oxide of palladium is formed on the wire, but it appears not to interfere with the extraction and oxidation of the hydrogen. The wire measured,

		Difference.
Before charge	443·25 millims.	
With hydrogen	449·90 ,,	+6·65 millims.
After discharge	437·31 ,,	—5·94 ,,

The retraction of the wire therefore does not require the concurrence of a high temperature. This experiment further proved that a large charge of hydrogen may be removed in a complete manner by exposure to the positive pole (for four hours in this case) ; for the wire in its ultimate state gave no hydrogen on being heated *in vacuo*.

That particular wire, which had been repeatedly charged with hydrogen, was once more exposed to a maximum charge, for the purpose of ascertaining whether or not its elongation under hydrogen might now be facilitated and become greater in consequence of the previous large retraction. No such extra elongation, however, was observed on charging the retracted wire more than once ; and the expansion continued to be in the usual proportion to the hydrogen absorbed. The final density of the wire was 12·18.

The wire retracted by heat is found to be altered in another way, which appears to indicate a molecular change. When the gas has been expelled by heat, the metal gradually loses much of its power to take up hydrogen. The last wire, after it had already been operated upon six times, was again charged with hydrogen for two hours, and was found to occlude only 320 volumes of gas, and in a repetition of the experiment, 330·5 volumes. The absorbent power of the palladium had therefore been reduced to about one-third of its maximum.

The condition of the retracted wire appeared, however, to be improved by raising its temperature to full redness by sending through it an electrical

current from a battery. The absorption rose thereafter to 425 volumes of hydrogen, and in a second experiment to 422·5 volumes.

The wire becomes fissured longitudinally, acquires a thready structure, and is much disintegrated on repeatedly losing hydrogen, particularly when the hydrogen has been extracted by electrolysis in an acid fluid. The palladium in the last case is dissolved by the acid to some extent. The metal appeared, however, to recover its full power to absorb hydrogen, now condensing upwards of 900 volumes of gas.

The effect upon its length of simply annealing the palladium wire by exposure in a porcelain tube to a full red heat, was observed. The wire measured 556·075 millims. before, and 555·875 millims. after heating; or a minute retraction of 0·2 millim, was indicated. In a second annealing experiment, with an equal length of new wire, no sensible change whatever of length could be discovered. There is no reason, then, to ascribe the retraction after hydrogen, in any degree, to the heat applied when the gas is expelled. Palladium wire is very slightly affected in physical properties by such annealing, retaining much of its first hardness and elasticity.

2. *Tenacity*.—A new palladium wire, similar to the last, of which 100 millims. weighed 0·1987 grm., was broken, in experiments made on two different portions of it, by a load of 10 and of 10·17 kilogrammes. Two other portions of the same wire, fully charged with hydrogen, were broken by 8·18, and by 8·27 kilogrammes. Hence we have—

Tenacity of palladium wire 100

Tenacity of palladium and hydrogen 81·29

The tenacity of the palladium is reduced by the addition of hydrogen, but not to any great extent. It is a question whether the degree of tenacity that still remains is reconcileable with any other view than that the second element present possesses of itself a degree of tenacity such as is only found in metals.

3. *Electrical Conductivity*.—Mr. Becker, who is familiar with the practice of testing the capacity of wires for conducting electricity, submitted a palladium wire, before and after being charged with hydrogen, to trial, in comparison with a wire of German silver of equal diameter and length, at 10°·5. The conducting-power of the several wires was found as follows, being referred to pure copper as 100 :—

Pure copper 100

Palladium 8·10

Alloy of 80 copper + 20 nickel 6·63

Palladium + hydrogen 5·99

A reduced conducting-power is generally observed in alloys, and the charged palladium wire falls 25 per cent. But the conducting-power remains still considerable, and the result may be construed to favour the metallic character of the second constituent of the wire. Dr. Matthiessen confirms these results.

4. *Magnetism*.—It is given by Faraday as the result of all his experiments, that palladium is “feebly but truly magnetic;” and this element he placed at the head of what are now called the paramagnetic metals. But the feeble magnetism of palladium did not extend to its salts. In repeating such experiments, a horseshoe electromagnet of soft iron, about 15 centims. (6 inches) in height, was made use of. It was capable of supporting 60 kilogs., when excited by four large Bunsen cells. This is an induced magnet of very moderate power. The instrument was placed with its poles directed upwards; and each of these was provided with a small square block of soft iron terminating laterally in a point, like a small anvil. The palladium under examination was suspended between these points in a stirrup of paper attached to three fibres of cocoon silk, 3 decimetres in length, and the whole was covered by a bell glass. A filament of glass was attached to the paper, and moved as an index on a circle of paper on the glass shade divided into degrees. The metal, which was an oblong fragment of electro-deposited palladium, about 8 millims. in length and 3 millims. in width, being at rest in an equatorial position (that is, with its ends averted from the poles of the electromagnet), the magnet was then charged by connecting it with the electrical battery. The palladium was deflected slightly from the equatorial line by 10° only, the magnetism acting against the torsion of the silk suspending thread. The same palladium charged with 604.6 volumes of hydrogen was deflected by the electromagnet through 48° , when it set itself at rest. The gas being afterwards extracted, and the palladium again placed equatorially between the poles, it was not deflected in the least perceptible degree. The addition of hydrogen adds manifestly, therefore, to the small natural magnetism of the palladium. To have some terms of comparison, the same little mass of electro-deposited palladium was steeped in a solution of nickel, of sp. gr. 1.082, which is known to be magnetic. The deflection under the magnet was now 35° , or less than with hydrogen. The same palladium being afterwards washed and impregnated with a solution of protosulphate of iron of sp. gr. 1.048, of which the metallic mass held 2.3 per cent. of its weight, the palladium gave a deflection of 50° , or nearly the same as with hydrogen. With a stronger solution of the same salt, of sp. gr. 1.17, the deflection was 90° , and the palladium pointed axially.

Palladium in the form of wire or foil gave no deflection when placed in the same apparatus, of which the moderate sensitiveness was rather an advantage in present circumstances; but when afterwards charged with hydrogen, the palladium uniformly gave a sensible deflection of about 20° . A previous washing of the wire or foil with hydrochloric acid, to remove any possible traces of iron, did not modify this result. Palladium reduced from the cyanide and also precipitated by hypophosphorous acid, when placed in a small glass tube, was found to be not sensibly magnetic by our test; but it always acquired a sensible magnetism when charged with hydrogen.

It appears to follow that hydrogenium is magnetic, a property which is confined to metals and their compounds. This magnetism is not perceptible in hydrogen gas, which was placed both by Faraday and by M. E. Becquerel at the bottom of the list of diamagnetic substances. This gas is allowed to be upon the turning-point between the paramagnetic and diamagnetic classes. But magnetism is so liable to extinction under the influence of heat, that the magnetism of a metal may very possibly disappear entirely when it is fused or vaporized, as appears to be the case with hydrogen in the form of gas. As palladium stands high in the series of the paramagnetic metals, hydrogenium must be allowed to rise out of that class, and to take place in the strictly magnetic group, with iron, nickel, cobalt, chromium, and manganese.

5. *Palladium with Hydrogen at a high Temperature.*—The ready permeability of heated palladium by hydrogen gas would imply the retention of the latter element by the metal even at a bright red heat. The hydrogenium must in fact travel through the palladium by cementation, a molecular process which requires time. The first attempts to arrest hydrogen in its passage through the red-hot metal were made by transmitting hydrogen gas through a metal tube of palladium with a vacuum outside, rapidly followed by a stream of carbonic acid, in which the metal was allowed to cool. When the metal was afterwards examined in the usual way, no hydrogen could be found in it. The short period of exposure to the carbonic acid seems to have been sufficient to dissipate the gas. But on heating palladium foil red-hot in a flame of hydrogen gas, and suddenly cooling the metal in water, a small portion of hydrogen was found locked up in the metal. A volume of metal amounting to 0.062 cubic centim., gave 0.080 cubic centim. of hydrogen; or, the gas, measured cold, was 1.306 times the bulk of the metal. This measure of gas would amount to three or four times the volume of the metal at a red heat. Platinum treated in the same way appeared also to yield hydrogen, although the quantity was too small to be much relied upon, amounting only to 0.06 volume of the metal. The permeation of these metals by hydrogen appears therefore to depend on absorption, and not to require the assumption of anything like porosity in their structure.

The highest velocity of permeation observed was in the experiment where four litres of hydrogen (3992 cub. centims.) per minute passed through a plate of palladium 1 millim. in thickness, and calculated for a square metre in surface, at a bright red heat a little short of the melting-point of gold. This is a travelling movement of hydrogen through the substance of the metal with the velocity of 4 millimetres per minute.

6. *Chemical Properties.*—The chemical properties of hydrogenium also distinguish it from ordinary hydrogen. The palladium alloy precipitates mercury and calomel from a solution of the chloride of mercury without any disengagement of hydrogen; that is, hydrogenium decomposes chloride of mercury, while hydrogen does not. This explains why M. Stanislas

Meunier failed in discovering the occluded hydrogen of meteoric iron, by dissolving the latter in a solution of chloride of mercury; for the hydrogen would be consumed, like the iron itself, in precipitating mercury. Hydrogen (associated with palladium) unites with chlorine and iodine in the dark, reduces a persalt of iron to the state of protosalt, converts red prussiate of potash into yellow prussiate, and has considerable deoxidizing powers. It appears to be the active form of hydrogen, as ozone is of oxygen.

The general conclusions which appear to flow from this inquiry are, that in palladium fully charged with hydrogen, as in the portion of palladium wire now submitted to the Royal Society, there exists a compound of palladium and hydrogen in a proportion which may approach to equal equivalents*. That both substances are solid, metallic, and of a white aspect. That the alloy contains about 20 volumes of palladium united with a volume of hydrogenium; and that the density of the latter is about 2, a little higher than magnesium to which hydrogenium may be supposed to bear some analogy. That hydrogenium has a certain amount of tenacity, and possesses the electrical conductivity of a metal. And finally, that hydrogenium takes its place among magnetic metals. The latter fact may have its bearing upon the appearance of hydrogenium in meteoric iron, in association with certain other magnetic elements.

I cannot close this paper without taking the opportunity to return my best thanks to Mr. W. C. Roberts for his valuable cooperation throughout the investigation.

II. "A Memoir on the Theory of Reciprocal Surfaces."

By Professor CAYLEY, F.R.S. Received November 12, 1868.

(Abstract.)

The present Memoir contains some extensions of Dr. Salmon's theory of Reciprocal Surfaces. I wish to put the formulæ on record, in order to be able to refer to them in a "Memoir on Cubic Surfaces," but without at present attempting to completely develop the theory.

Dr. Salmon's fundamental formulæ (A), (B) are replaced by

$$a(n-2) = \kappa - B + \rho + 2\sigma,$$

$$b(n-2) = \rho + 2\beta + 3\gamma + 3t,$$

$$c(n-2) = 2\sigma + 4\beta + \gamma + \theta,$$

$$a(n-2)(n-3) = 2(\delta - C) + 3(ac - 3\sigma - \chi) + 2(ab - 2\rho - j),$$

$$b(n-2)(n-3) = 4k + (ab - 2\rho - j) + 3(bc - 3\beta - \gamma - i),$$

$$c(n-2)(n-3) = 6h + (ac - 3\sigma - \chi) + 2(bc - 3\beta - \gamma - i),$$

where j , θ , χ , B , C refer to singularities not taken account of in his theory; viz. j is the number of pinch-points on the nodal curve θ , χ , the numbers of certain singular points on the cuspidal curve, C the number of conic nodes, B the number of biplanar nodes: the reciprocal singularities j' , θ' , χ' ,

* Proceedings of the Royal Society, 1868, p. 425.